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RAPID EVALUATION OF THE WORKABILITY OF CONTAINER GLASS

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A program is developed for estimating the workability characteristics of container glasses. An accuracy of estimated values comparable to the experimental accuracy was possible due to the chosen algorithm and the use of correction coefficients established on the basis of a substantial database on compositions and properties of container glasses.

In spite of strong competition from other kinds of packaging, glass packaging still remains the most mass-scale product of the world glass industry, which comprises almost 2/3 of the total volume of produced glass and tends to grow.

Problems of process intensification, improvement of quality, and reducing production cost are very important for Russian manufacturers of glass containers, who aspire to assume leading positions in the Russian and world market.

The basis for the technological solution of the above listed problems is the appropriate selection of the optimum chemical composition of glass that would combine the following characteristics:

– a high value of the temperature gradient for viscosity and solidification rate, to ensure the efficient operation of contemporary glass-molding machines;

– a sufficiently wide interval of safe molding excluding the possibility of crystallization of the glass melt inside the tank furnace and the feeder;

– reliable service properties of the product (heat resistance, strength, and chemical resistance);

– the possibility of rational application of raw materials.

When selecting the optimum chemical composition for container glass, one should take into account a set of general requirements [1] and the actual production conditions. In this context, each manufacture needs a system of rapid and reliable evaluation of the advantages and disadvantages of a particular chemical composition of container glass, in order to be able to effectively improve the compositions and to make a choice. Such problems currently arise in connection with the replacement of glass-molding machinery and materials, as well as increased requirements on the quality and service reliability of glass containers, the need to expand the product range, to raise the efficiency, etc.

The determining criteria for the technological effectiveness of a container glass composition are the temperature dependence of viscosity and a set of workability indices proposed by the Emhart company [1] estimated on the basis of this dependence.

The parameter proposed as the main workability index is the relative speed of the glass-molding machine (the English abbreviation: RMS) calculated using the Littleton t_L and vitrification t_g characteristic temperatures and expressed in percent:

$$\mathrm{RMS} = \frac{(t_L - 450)\times 100}{t_L - t_g + 80}.$$

RMS values exceeding 100% indicate the acceptability of the considered glass composition for molding glass articles on high-speed machines.

The drop temperature correlates with a viscosity of 10^2 Pa · sec.

The workability index WR determines the molding temperature interval and is calculated from the formula

$$\mathrm{WR} = t_d - t_L.$$

The relative "length" of glass (English abbreviation WRI) is calculated as follows:

$$\mathrm{WRI} = t_L - t_g.$$

This index, which determines the temperature interval of article shape fixation, in most industrially produced container glasses exceeds 160°C.

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TABLE 1

Year	Weight content, %			RMS, %
	SiO_2	$RO + R_2O_3$	R_2O	
1950	72.1	12.5	15.5	103.0
1964	72.0	13.1	15.0	104.0
1972	72.4	13.2	14.7	106.0
1977	72.2	13.3	14.4	107.0
1998	72.0	14.0	14.0	108.5

Of special significance in a highly efficient glass-molding process is the index estimating the possibility of glass crystallization (English abbreviation DI):

$$DI = WRI - 160.$$

When the DI value is positive, the danger of glass crystallization in the course of molding is excluded, and when this value is negative, the glass may become crystallized in the feeder.

It should be noted that the characteristics temperatures (except for t_d), which serve as the basis for the calculation of the workability indices, can be easily and accurately determined experimentally in an industrial laboratory. However, the optimization of chemical compositions implies a comparative evaluation of numerous glasses that differ in their component ratios. Obviously, rapid execution of such work is possible when employing a computer and a reliable software product for the calculation of the optimization criteria, which could yield a result comparable in reliability and accuracy to the experimental results.

The determination of the characteristic temperatures and the calculation of the workability indices of container glass is based on the temperature dependence of glass viscosity. It is known [2, 3] that unlike other glass properties, viscosity has a complex relationship with the chemical composition of glass and temperature. Therefore, universal methods of calculation, which would encompass wide composition ranges and provide satisfactory accuracy, are absent. Methods based on the additivity rule can be used only when the variations of glass compositions are limited, which is typical of container glasses.

In the present study, the temperatures related to certain values of viscosity of container glasses with various chemical compositions were determined using the methods developed by Okhotin and Mazurin, Tret'yakova, and Shvaiko-Shvaikovskaya [4, 5]. The calculated values of the characteristic temperatures (drop, Littleton, and vitrification temperatures) were compared with the experimentally obtained values. The experimental data bank included the chemical compositions and technological characteristics of 80 container glasses [1, 6 – 8]. It was observed that the calculations according to the Okhotin method yield more precise results, i.e., agree to a greater extent with the experimental data. This is accounted for by the general regularity that is true for all properties: the more narrow the range of compositions encompassed by a certain calculation method, the more accurate the calculation is. That is why further processing was performed on the data obtained according to the Okhotin method. The estimated temperatures were corrected taking into account the presence of barium oxide in the glass composition, using the Helhoff and Thomas tables [2].

The estimated values in the high viscosity range (viscosity was measured in Pa · sec) corresponding to the temperatures of vitrification ($\log \eta = 12.3$) and annealing ($\log \eta = 12$) exceeded the experimental values by 4 – 7°C, which corresponds to $\Delta\log \eta = 0.20 – 0.35$. The deviations of the estimated data from the experimental ones (the error) in the range of the Littleton and the drop temperature comprised $+ 8 \div - 20$°C ($+ 0.15 \div - 0.57\ \Delta\log \eta$) and $+ 8 \div - 10$°C ($+ 0.034 \div - 0.043\ \Delta\log \eta$), respectively.

To estimate the value of error, the obtained viscosity values were compared with the precision of their experimental determination. The reproducibility of measurement results in the classic viscosity studies varied in the limit of $\Delta\log \eta = \pm 0.03$ from one sample to another. While studying the samples produced in different meltings, the specified value as a rule grew significantly ($\Delta\log \eta$ reached ± 0.1). The spread in the viscosity values was even more significant when comparing the data supplied by different researchers [2].

The precision of determination significantly depends on the viscosity temperature gradient. The effect of the temperature on the viscosity of silicate glass melts is not great. Usually the temperatures corresponding to the viscosity 10 and 10^2 Pa · sec differ by 250 – 300°C. With such a low viscosity gradient, the error in determining the characteristic temperatures corresponds to a quite acceptable error $\Delta\log \eta$. At the same time, the temperature difference corresponding to the viscosity logarithm $10^{11} – 10^{12}$ Pa · sec is 20 – 25°C. The high value of the viscosity gradient determines a significant increase in the estimation error $\Delta\log \eta$ in the specified temperature range [2].

As the result, the error in estimating t_L and t_g of container glasses exceeded 2 – 5 times the error of the experimental determination and surpassed the admissible interval limits, since the workability index values significantly depend on these temperatures. Thus, a change by 1°C in t_g results in a change in the RMS by 0.4%; consequently, its estimated values exceeded the actual parameters on the average by 2 – 3%. It is evident that the obtained deviations in the RMS values are inadmissible, as they reflect a significant variation in the glass composition.

It can be noted that for the past 50 years, the chemical compositions of container glasses were mostly refined by replacing their R_2O content with RO, which led to a substantial improvement of service properties and increased the RMS from 103 to 107 – 108% (Table 1) [7].

To increase the accuracy of estimating the main characteristic temperatures, the correction coefficients were determined in statistical processing of the obtained data. The re-

TABLE 2

Country	Weight content in decolorized glass, %				
	SiO_2	Al_2O_3	MgO	CaO	Na_2O
USSR	71.96	2.80	3.71	6.00	14.85
USA	72.41	1.96	0.99	10.00	14.28

fined values of the characteristic temperatures were used to calculate the constants A, B, and t_0 in the Fogel – Fulcher – Tamman (FFT) equation of temperature dependence of viscosity for specific glass compositions. The accuracy of the calculation of viscosity $\log \eta = A + B/(t - t_0)$ or temperature $t = t_0 + B/(\log \eta - A)$ based on the FFT equation in the known technological interval and, accordingly, the calculation of the workability indices was comparable with the accuracy of experimental determination. For instance, the mean quadratic deviation of the estimated vitrification temperature from the experimental value was + 2.4°C, which corresponds to $\Delta\log \eta = 0.12$.

The error level accomplished in estimating the vitrification temperature can be appraised in the context of the effect of the chemical composition of glass on its vitrification temperature. Such increase in the value of t_g is equivalent, for instance, to the effect produced by the substitution of RO for R_2O or Al_2O_3 for SiO_2 in the amount of 0.2 and 0.5 wt.%, respectively. It should be noted that such deviations in the component composition do not go beyond the limits of the acceptable standards in accordance with OST 21-51–97. Consequently, variations in t_g within the accomplished error limits may occur in using glass of the same grade at any glass factory. Therefore, the accomplished degree of precision can be regarded as quite satisfactory.

The performed studies were used to develop a program for estimating the temperature dependence of viscosity, the characteristic temperatures, and the workability indices of container glasses. The algorithm of this program provides estimated values comparable to the experimental data.

The program makes it possible to perform calculations for container glasses with the following composition (%): 12 – 16 Na_2O (including 0 – 2 K_2O), 0 – 5 MgO, 5 – 12 CaO, 0 – 2 BaO, 0 – 5 Al_2O_3, 0 – 0.5 Fe_2O_3, and 0 – 0.5 SO_3.

The calculation yields the following results: FFR equation of temperature dependence of viscosity, the drop, Littleton, and vitrification characteristic temperatures, and workability indices RMS, WR, WRI, and DI. Any user can at will obtain the tabulated dependence of viscosity on temperature with a temperature variation interval of 10°C and thus calculate the viscosity (temperature) for any given value of temperature (viscosity).

TABLE 3

Parameter	Glass BT-1	
	USSR	USA
FFT equation	$\log \eta = -2.37 + 4302/(t - 244)$	$\log \eta = -1.91 + 3432/(t - 313)$
Temperature, °C:		
drop	1229	1194
Littleton	731	734
vitrification	532	545
Workability indices:		
RMS, %	100.8	105.6
WR, °C	497	460
WRI, °C	199	189
DI, °C	39	29

By way of example, Tables 2 and 3 show the results of estimating the technological characteristics of averaged container glass compositions produced in the USSR and the USA (1977) [7].

The represented set of technological parameters evidently demonstrates the advantages and disadvantages of the particular glass compositions.

The developed software product is accessible for use on any PC, operates in Window OS, and has a convenient interface.

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